PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Process for the Production of Organic Isocyanates

We, GOSUDARSTVENNY NAUCHNO-ISSLEDOVATELSKY I PROEKTNY INSTITUT AZOTNOY PROMYSHLENNOSTI I PRODUKTOV ORGANICHESKOGO SINTEZA, of ulitsa Chkalova, 50 Moscow-ZH-28, Union of Soviet Socialist Republics a body corporate of the Union of Soviet Socialists Republics, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for the production of organic isocyanates by phosgenating organic amines.

According to a known method for producing organic isocyanates, a solution of an amine is reacted with a solution of phosgene in an organic solvent in a circulating reaction mixture. This process can be performed continuously at a pressure of up to 14 atmospheres and at a temperature of up to 180° in a tubular reactor, and involves repeated recirculation of the reaction products in the system, with periodic additions of fresh phosgene and of the amine solution.

In this prior art process, it is usual to commence the discharge of the reaction mixture, for the purpose of separating the isocyanate, from 3 to 5 hours after the first addition of phosgene and amine solution to the pure solvent circulating in the system, and when the concentration of the isocyanate in the system reaches 8—10%.

However, this process is useful primarily for the preparation of aromatic isocyanates. Its employment for the preparation of aliphatic isocyanates presents difficulties, since, under the conditions of the reaction, aliphatic amines react with phosgene to give highly reactive carbamoyl chlorides which immediately react with a further molecule of amine to give substituted ureas: the latter compounds being incapable of further reaction with phosgene under the conditions used.

The above process suffers from the further disadvantage of maintaining the isocyanate at elevated temperatures for a considerable period of time, thereby promoting polymerization and polycondensation of the isocyanate product.

High-temperature phosgenation at moderate pressure and low phosgene concentrations in the reaction mixture is conducive to the formation of amine hydrochlorides and substituted ureas and involves side reactions, such as the deamination of amine hydrochlorides and formation of allophanic acid derivatives and biuret.

The invention consists in a process for the production of organic isocyanates from an amine and phosgene, in which the amine, preheated to a temperature below its decomposition temperature, is caused to react with phosgene, preheated to a temperature above its critical temperature, the temperature of the reaction system being maintained at or above the temperature at which commences dissociation of the hydrochloride of said amine and the pressure being maintained at or above the pressure required to keep all of the components of the reaction system in the liquid phase.

Preferably, the process of the invention is effected in a continuous, through-flow reactor, such as a tubular reactor.

Since the phosgene and amine undergo separate preheating, the exothermic phosgene transition from supercriticality to the liquid phase is useful in attaining the high temperature at which the reaction mixture components are contacted, and is also useful in controlling, within reasonable limits, the extent of amine preheating which is necessary.

The amine used in the invention should preferably be a primary amine which contains no groups capable of reacting with phosgene, other than the NH_2-group. The amine may be used in the liquid state or as a solution or suspension in an inert organic solvent. It is also possible to employ a mixture of amines in an inert solvent: this is especially useful if the starting amine exhibits low solubility or does not lend itself to being suspended in an inert solvent, when the desired amine is dissolved in another primary amine and an inert solvent is added to the mixture. The second amine component should be selected so that isocyanates obtained from the two amines are readily separable from each other by distillation or fractionation.

It is preferred that the reaction be performed at a temperature above 180° C; the pressure in the reactor being maintained in the 20 to 150 atmosphere range, depending upon the properties of the inert solvent used.

The amount of phosgene used in the process should preferably be 2.5 to 5.5 times the stoichiometric equivalent.

The unconverted excess phosgene and any organic solvent used are preferably recycled after the separation of the reaction products.

The dwell time of the reactants in the reaction zone should preferably not exceed 5 to 60 seconds, the precise time depending upon the nature of the starting amine. When the amine is subjected to phosgenation in the absence of a solvent, the duration of the process may be somewhat increased.

When the amines are subjected to phosgenation in a solution or suspension, the solvent used is an inert organic solvent, such as benzene, toluene, xylene, chlorobenzene, o-dichlorobenzene or trichlorobenzene. In order to achieve the desired solubility of phosgene in solvents that boil at a lower temperature than does chlorobenzene, higher pressures are required; whilst where use is made of higher boiling solvents, it is feasible to resort to a lower pressure than that used in conjunction with chlorobenzene. These considerations have found adequate experimental corroboration.

In a preferred embodiment, the reactants are introduced to the bottom of a through-flow tubular reactor by any technique that ensures intimate contact between the phosgene and the amine feed, but it is most preferable to use opposed reagent streams, the angle between the streams being, preferably, 180 deg.

Apart from being used to prepare known isocyanates, the invention has also been used to phosgenate amines from which no isocyanates have heretofore been prepared: viz. 1,3 - diamino - cyclohexane (cis) 1,4 - diaminocyclohexane (trans), 4,4′ - diamino - diphenylethane, 4,4′ - diamino - 2,2′ - dichlorodiphenylmethane, and 4,4′ - diamino - 3,5,3′,5′ - tetramethyldiphenyl.

The following novel diisocyanates have been obtained: cyclohexane - 1,3 - diisocyanate (cis); b.p. 140° C/23 mm, n_D^{20} 14809; cyclohexane - 1,4 - diisocyanate (trans); b.p. 145—146°C/32 mm; cryst. temp., 58.5°C; diphenylethane-4,4′-diisocyanate; b.p. 184°C/2 mm; m.p. 88.5°C; 2,2′ - dichlorodiphenylmethane - 4,4′ - diisocyanate; b.p. 181—182° C/1 mm; m.p. 105°C; 3,5,3′,5′ - tetramethyldiphenyl - 4,4′ - diisocyanate, b.p. 168—619°C/1 mm; m.p. 78°C.

A combination of high temperature conditions and a high phosgene concentration in the reaction mixture results in a marked diminution of the duration of the process for isocyanate production, inhibits the reactions leading to the formation of intermediate products, such as amine hydrochlorides and substituted ureas, and decreases the yield of secondary by-products, thereby making it possible to synthesize diverse mono-, di- or polyisocyanates from amines and phosgene with high yields, using a single temperature and per single pass.

The invention is further described in the reference to an embodiment illustrated in the accompanying drawing, which shows a flow diagram for the process.

In the drawing, the liquid phosgene from container 1 is fed continuously via pipeline 2 to metering pump 3, which delivers it through pipeline 4 to thermostatted heater 5, where the phosgene is heated to a supercritical temperature and thereafter delivered via pipeline 6 to the bottom of thermostatted through-flow tubular reactor 7. The amine, or a solution or suspension thereof in an inert organic solvent, is fed continuously from container 8 via pipe line 9 to metering pump 10, which delivers it through pipeline 11 to thermostatted heater 12, where the amine is heated to a temperature below its decomposition temperature, and thereupon delivered via pipeline 13 to the bottom of thermostatted reactor 7, in the same manner as the phosgene.

The desired pressure is maintained in reactor 7 by discharging continuously the reaction products from the reactor via pipeline 14 through throttling valve 15 into separator 16, in which the main bulk of hydrogen chloride and unconverted phosgene is separated from the crude isocyanate product at atmospheric or slightly higher pressure.

The crude isocyanate thus obtained leaves separator 16 via pipeline 17, is purged with an inert gas at an elevated temperature to remove the residual dissolved phosgene and

hydrogen chloride, and thereafter the pure isocyanate is separated by conventional techniques.

When the process is carried out in an inert solvent, the solvent is separated from the isocyanate product by distillation or rectification and the recovered solvent is recycled to prepare the starting solution or suspension of the primary amine.

The mixture of phosgene vapour and hydrogen chloride that emerges from separator 16 is directed via pipeline 18 to low-temperature condenser 19, in which the bulk of the phosgene undergoes condensation, whilst the hydrogen chloride with an admixture of phosgene is delivered through pipeline 20 to a neutralization step. The liquid phosgene that collects in condenser 19 flows to collecting tank 21 and thereafter is delivered via pipeline 22 to container 1.

The invention is further illustrated by the following Examples

EXAMPLE 1

2,000 ml of a chlorobenzene solution of hexamethylenediamine containing 205 g of hexamethylenediamine are delivered continuously and at a constant rate for a period of one hour to a 25-ml reactor, the solution being preheated in a heater maintained at a temperature of 216—219°C. Simultaneously with the stream of the hexamethylenediamine solution there is passed through the reactor continuously and at a constant rate 1,680 g of phosgene preheated in a heater maintained at 220—224°C. The reactor is thermostatted at a temperature of 218—220°C. In the reaction zone, the temperature is 233—235°C, whilst the pressure in the reactor is maintained at 60—62 atmospheres. The reaction products are continuously discharged into a separator. To remove phosgene and hydrogen chloride, the crude hexamethylenediisocyanate solution thus obtained is purged with a stream of dry nitrogen heated to 110—125°C. Fractionation of the crude product in vacuo gives 265 g of hexmethylenediisocyanate; b.p. 105—106°C/3 mm Hg; n_D^{20} 1.4530. The yield is 89% of theoretical based on the hexamethylenediamine used.

EXAMPLE 2

Following the procedure described in Example 1, 1,500 ml of a chlorobenzene solution containing 150 g decamethylenediamine and 840 g of phosgene are passed through the reactor for a period of one hour, to give 170 g of decamethylenediisocyanate; b.p. 140—142°C/3 mm Hg; n_D^{20} 1.4564. Yield 87%.

EXAMPLE 3

Following the procedure described in Example 1, 1,560 ml of a chlorobenzene solution of 150 g toluenediamine (65% of 2,4 - isomer and 35% of 2,6 - isomer), preheated in the amine heater maintained at 174—178°C, and 1,256 g of phosgene, preheated in the phosgene heater maintained at 216—220°C, are passed during one hour through the reactor thermostatted at 220—225°C, the temperature in the reaction zone being 220—223°C and the pressure in the reactor 50—54 atmospheres.

The reaction gives 202 g of toluenediisocyanate (65% of 2,4 - isomer and 35% of 2,6 - isomer); b.p. 101—102° C/5 mm Hg; n_D^{20} 1.5676. Yield 94.3%.

EXAMPLE 4

Following the procedure described in Example 3, 1,825 ml of a chlorobenzene solution of 158 g 2,4 - diaminochlorobenzene and 1,120 g of phosgene are passed through the reactor for a period of one hour. The reactor is thermostatted at a temperature of 235—240°C, the temperature in the reaction zone being 210—215°C.

The reaction gives 195 g of chlorobenzene-2,4 - diisocyanate; b.p. 145—146°C/23 mm Hg; m.p. 65—67°C. Yield 90.5%.

EXAMPLE 5

Following the procedure described in Example 1, 2,600 ml of a suspension prepared from 200 g of 1,5-diamino-naphthalene and chlorobenzene and preheated in a heater maintained at 221—223°C and 1,250 g of phosgene preheated in a heater maintained at 226—230°C are passed for a period of one hour through the reactor thermostatted at 230—235°C. In the reaction zone, the temperature is 220—225°C, and a pressure of 50—55 atmospheres is maintained in the reactor.

The reaction gives 233 g of naphthalene - 1,5 - diisocyanate; b.p. 220—221°C/40 mm Hg; m.p. 130—131°C. Yield 87.6%.

EXAMPLE 6

Following the procedure described in Example 1, 3,000 ml of a chlorobenzene solution of 1,395 g *m* - chloroaniline (heater temperature, 165—170°C) and 2,800 g of phosgene (heater temperature, 185—190°C) are passed for a period of one hour through the reactor thermostatted at 195—200° C. In the reaction zone, the temperature is 195—200°C and a pressure of 52—56 atmospheres is maintained in the reactor.

The reaction yields 1,600 g of *m* - chlorophenylisocyanate; b.p. 103—104°C/30 mm Hg; n_D^{20} 1.5578. Yield 95.2%.

EXAMPLE 7

Following the procedure described in Example 1, 1,350 ml of a chlorobenzene solution of 200 g aniline (heater temperature, 215—218°C) and 850 g of phosgene (heater temperature, 220—225° C) are passed for a period of one hour through the reactor ther-

mostatted at 218—222°C. In the reaction zone the temperature is 215—225°C and a pressure of 60—62 atmospheres is maintained in the reactor.

The reaction gives 243 g of phenylisocyanate; b.p. 55—57°C/16 mm Hg; Yield 95%.

Example 8

Following the procedure described in Example 7, 365 g of aniline and 700 g of phosgene are passed through the reactor for a period of one hour, the temperature in the reaction zone being 231—234°C and the pressure in the reactor 50—51 atmospheres.

The reaction gives 303 g of phenylisocyanate; b.p. 55—57°C/16 mm Hg. Yield 65%.

Example 9

Following the procedure described in Example 1, 2,380 ml of a chlorobenzene solution of 191 g 4,4′ - diaminodiphenylmethane (heater temperature, 200—205°C) and 750 g of phosgene (heater temperature, 220—224°C) are passed for a period of one hour through the reactor thermostatted at 215—200°C, the pressure in the reactor being maintained at 50—60 atmospheres. The temperature in the reaction zone is 215—220°C.

The reaction gives 225 g of diphenylmethane - 4,4′ - diisocyanate; b.p. 187—188°C/2 mm Hg; m.p. 37—38°C. Yield 93.7%.

Example 10

Following the procedure described in Example 9, 2,300 ml of a chlorobenzene solution of 180 g 4,4′ - diamino - α,β - diphenylethane and 850 g of phosgene are passed through the reactor during one hour.

The reaction gives 191 g of α,β - diphenylethane - 4,4′ - diisocyanate; b.p. 184—185°C/2 mm Hg; m.p. 88°C. Yield 85%.

Example 11

Following the procedure described in Example 9, 2,000 ml of a chlorobenzene solution of 130 g 4,4′ - diamino - 3,5,3′,5′ - tetramethylenediphenylmethane and 500 g of phosgene are passed through the reactor for a period of one hour.

The reaction gives 142 g of 3,5,3′,5′ - tetramethyl - diphenylmethane - 4,4′ - diisocyanate; b.p. 177—178°C/1 mm Hg; m.p. 130—131°C. Yield 91%.

Example 12

Following the procedure described in Example 1, 3,000 ml of a chlorobenzene solution of 290 g 4,4′ - diamino - 2,2′ - dichlorodiphenylmethane (heater temperature, 190—195°C) and 1,100 g of phosgene (heater temperature, 222—227°C) are passed during one hour through the reactor thermostatted at 230—235°, the temperature in the reaction zone being 218—220°C. The pressure in the reactor is maintained at 50—52 atmospheres.

The reaction yields 287 g of 2,2′ - dichlorodiphenyl - methane - 4,4′ - diisocyanate; b.p. 181—182°C/1 mm Hg; m.p. 105°C. Yield 82.8%.

Example 13

Following the procedure described in Example 1, 1,000 ml of a chlorobenzene solution of 100 g 4,4′- diamino - dicyclohexylmethane (heater temperature, 223—225°C) and 450 g of phosgene (heater temperature, 228—230°C) are passed during one hour through the reactor thermostatted at 240—245° C, the temperature in the reaction zone being 245—250°C. The pressure in the reactor is maintained at 60—62 atmospheres.

The reaction yields 100 g of dicyclohexylmethane - 4,4′ - diisocyanate; b.p. 167—168°C/1.5 mm Hg; n_D^{20} 1,4977. Yield 80%.

Example 14

Following the procedure described in Example 13, 1,000 ml of a chlorobenzene solution of 100 g 1,3 - diamino - cyclohexane (cis) and 880 g of phosgene yield 110 g of cyclohexane - 1,3 - diisocyanate (cis); b.p. 140—140.5°C/23 mm Hg; n_D^{20} 1.4809. Yield 75.5%.

Example 15

Following the procedure described in Example 13, 1,000 ml of a chlorobenzene solution of 100 g 1,4 - diaminocyclohexane (trans) and 850 g of phosgene give 115 g of cyclohexane - 1,4 - diisocyanate (trans); b.p. 145—146°C/32 mm Hg; cryst. temp. 58.5°C. Yield 78.8%.

Example 16

Following the procedure described in Example 1, 1,520 ml of a solution containing 105 g of 4,4′,4″ - triaminotriphenylmethane (heater temperature, 215—220°C) and 580°C of phosgene (heater temperature, 225—228°C) are passed for a period of one hour through the reactor thermostatted at 230—235°C, the temperature in the reaction zone being 212—217°C. The pressure in the reactor is maintained at 50—55 atmospheres.

The reaction yields 123 g of triphenyl - methane - 4,4′,4″ - triisocyanate which is 99% pure. Yield 91%.

Example 17

Following the procedure described in Example 1, 1,070 ml of a chlorobenzene solution of 200 g 3,4 - dichloroaniline and of 81.5 g o-dianisidine (heater temperature, 193—197°C) and 880 g of phosgene (heater temperature) 204—206°C) are passed for a period of one hour through the reactor thermostatted at 208—212°C, the temperature in the reaction zone being 230—235°C. The pressure in the

reactor is maintained at 51—53 atmospheres.

Vacuum distillation of the reaction products yields 216.7 g (93.3% yield) of 3,4 - dichlorophenylisocyanate, b.p. 117—118°C/30 mm Hg, m.p. 43—44°C, and 72 g (73.3% yield) of 3,3 - dimethoxydiphenyl - 4,4' - diisocyanate, b.p. 210—211°C/3 mm Hg, m.p. 117—118°C.

WHAT WE CLAIM IS:—

1. A process for the production of organic isocyanates from an amine and phosgene, in which the amine, preheated to a temperature below its decomposition temperature, is caused to react with phosgene, preheated to a temperature above its critical temperature, the temperature of the reaction system being maintained at or above the temperature at which commences dissociation of the hydrochloride of said amine and the pressure being maintained at or above the pressure required to keep all of the components of the reaction system in the liquid phase.

2. A process according to claim 1, in which said amine is a primary amine.

3. A process according to Claim 2, in which said primary amine contains no groups other than NHC-groups capable of reacting with phosgene.

4. A process according to any preceding claim, in which the amine is a liquid amine.

5. A process according to any preceding claim, in which the amine is dissolved or suspended in an inert organic liquid.

6. A process according to claim 5, in which said amine is dissolved in another primary amine and said inert liquid is added to the mixed amines.

7. A process according to claim 5 or 6, in which said organic liquid is chlorobenzene, o-dichlorobenzene, benzene, toluene, xylene or trichlorobenzene.

8. A process according to any preceding claim, in which the reaction is performed at a temperature above 180°C.

9. A process according to any preceding claim, in which the pressure during the reaction is maintained at from 20 to 150 atmospheres.

10. A process according to any preceding claim, in which the amount of phosgene used in the reaction is from 2.5 to 5.5 times the stoichiometric equivalent with respect to the amine.

11. A process according to any preceding claim, in which the dwell time of the reactants in the reaction zone is from 5 to 60 seconds.

12. A process according to any preceding claim, in which the reaction is effected in a continuous, through-flow reactor.

13. A process according to Claim 12, in which said reactor is a tubular reactor.

14. A process according to any preceding claim, in which unconverted phosgene and any organic solvent used are separated from the reaction products and recycled for further reaction.

15. A process according to Claim 1, substantially as herein described with reference to the drawing.

16. A process according to claim 1, substantially as herein described with reference to any of the Examples.

17. A process according to Claim 1, in which the amine used is 1,3 - diaminocyclohexane (cis).

18. A process according to Claim 1, in which the amine used is 1,4 - diaminocyclohexane (trans).

19. A process according to Claim 1, in which the amine used is 4,4' - diamino - α,β - diphenylethane.

20. A process according to claim 1, in which the amine used is 4,4' - diamino - 2, 2' - dichlorodiphenylmethane.

21. A process according to claim 1, in which the amine used is 4,4' - diamino - 3,5,3',5' - tetramethyldiphenyl.

22. Cyclohexane - 1,3 - diisocyanate (cis).

23. Cyclohexane - 1,4 - diisocyanate (trans).

24. α,β - diphenylethane - 4,4' - diisocyanate.

25. 2,2' - Dichlorodiphenylmethane - 4,4' - diisocyanate.

26. 3,5,3',5' - Tetramethyldiphenyl - 4,4'- diisocyanate.

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1173890 COMPLETE SPECIFICATION

1 SHEET This drawing is a reproduction of the Original on a reduced scale